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Factors affecting the availability to radishes of cadmium added to soil

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Abstract. In a five week period, the cadmium uptake of radishes in pot experiments made in the greenhouse was on average 7.8 % of the cadmium mixed with the soil (0.4 mg Cd per 400 ml of soil). In a material consisting of samples from 25 plough layers the uptake varied from 1.4 to 11 % and in a material of samples from the corresponding subsoils from 1.4 to 22.6 %. The increase in cadmium content (Δ c) of the radish tops, which increase was regarded here as describing best the availability of added cadmium, varied in the plough layer material from 2.2 to 27.1 mg/kg and in the subsoil material from 4.3 to 94.9 mg/kg Cd on a dry matter basis. The increment Δ c was related to the amount of organic carbon (x_1) and to proportion of hydrogen (x_2)) of total exchangeable cations according to the equation $\Delta c = k \cdot \frac{x_2^{b_2}}{x_1^{b_1}}$. In this equation $0 < b_1 < 1$ and $0 < b_2 \leqq 1$. In the complete material of 50 soil samples, the coefficient of determination of the logarithmically transformed equation was $R^2 = 0.73$. The corresponding coefficient of determination in a material of plough layer samples ($R^2 = 0.48$) was imporoved when the increase in cadmium content of the radish tops grown in corresponding subsoil samples was included as an additional independent variable ($R^2 = 0.59$). This showed that some character other than any determined on the experimental soil was acting in the plough layer material.

According to present ideas, large amounts of cadmium in the human diet constitute a considerable risk to health (Friberg et al. 1974). Cadmium in the soil finds its way into the diet both directly in food plants and indirectly through fodder crops and animal products. The most important source of cadmium to plants is usually the soil, although considerable amounts may be deposited locally from the air (Lagerwerff and Specht 1971). In areas fertilized with sewage from settlements or industry, the soil is in particular danger of contamination (Linnman et al. 1973). In addition, some fertilizers contain cadmium levels which may increase the danger (Stenström and

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VAHTER 1974). The aim of this study was to clarify the effects of certain soil characteristics upon the availability of cadmium contaminating the soil.

Material and methods

The soil sample material consisted of 50 samples taken from 25 sites in various parts of South and East Finland. At each site samples were taken from the plough layer (topsoils) and below it to a depth of 40 cm (subsoils). The samples were allowed to reach an air-dry condition, and were ground to pass a 4 mm sieve.

A 400 ml sample of each soil was put into a plastic pot, and an equal quantity weighed into another pot. The pots were fertilized with

N	P	K	Mg	Mn	Cu	Zn	B	Mo	
10	2	3	2	0.05	0.05	0.05	0.05	0.002	mmol per pot.

To one of each pair of pots 0.4 mg of Cd were added as the nitrate. Water was added to the pots to give a soil water potential of pF 2.5. This tension was measured with a pressure plate apparatus. In each pots, four radish plants *(Raphanus sativus* L. cv. Non Plus Ultra) were grown from seed to 36 days old in a greenhouse during April and May 1973. The water lost was made up at intervals by watering the pots to their original weight.

The aerial (tops) and underground (roots) parts of the radish plants were harvested separately. The roots were freed from the soil by washing with deionized water. Yields were weighed air-dry. Subsamples were used for a dry matter determination at 105° C. After a wet combustion, the cadmium content was determined with a flameless atomic absorption spectrophotometer (Perkin Elmer). The cadmium uptakes were calculated from yields and their cadmium contents.

The following determinations were made on the experimental soils: pH in 0.01 M $CaCl_2$ suspension, organic carbon, clay ($<2\mu$m fraction), iron extractable in acid ammonium oxalate at pH 3.3, and also exchangeable hydrogen at pH 7 and cation exchange capacity in soils saturated with 1 N ammonium acetate. The amounts of organic carbon, clay, soluble iron and of exchangeable hydrogen and cation exchange capacity were calculated for the soil in each pot by multiplying the weight of soil by the corresponding content.

The statistical treatment of the results was based mainly on correlation and regression analyses. Since the linear regression equation $y = a + b_1x_1 + b_2x_2 + b_3x_3 + \ldots + b_kx_k$ embodies the assumption that the variables x_1, x_2, x_3 etc. define additive parts of y, parts independent of one another, and since this assumption is presumably not valid, it was decided to test another type of model. The linear regression equation $\log y = \log a' + b_1' \log x_1 + b_2' \log x_2 + b_3' \log x_3 + \ldots\ldots\ldots + b_k' \log x_k$ incorporating the logarithmically transformed variables was chosen for the test. When the independent variables (x) influence one another, this model is more logical. The equation can be expressed in the form $y = a' x_1^{b_1'} x_2^{b_2'} x_3^{b_3'} \ldots x_k^{b_k'}$, in which it is clear that the relative effect of each variable is assumed to be independent of the effect of other variables.

Table 1. Amounts and variation ot some characters determined on experimental soils.

	Topsoils n = 25		Subsoils n = 25		Whole material n = 50	
	mean	standard deviation	mean	standard deviation	mean	standard deviation
soil, g/pot	385	60	466	47	425	67
org. C, g/pot	17.7	8.7	4.0	2.9	10.9	9.4
clay (< 2 μm), g/pot	134	85	177	117	155	104
CEC, mval/pot	129	48	113	53	121	51
exch. H, mval/pot	72	19	57	19	65	20
Fe, soluble in ammonium oxalate, g/pot	3.62	1.99	3.73	2.30	3.67	2.13
pH_{CaCl_2}	4.9	0.46	5.1	0.55	5.0	0.51

Table 2. Dry matter yield, its cadmium content and cadmium uptake of radish without added cadmium.

	Topsoils n = 25		Subsoils n = 25		Whole material n = 50	
	mean	standard deviation	mean	standard deviation	mean	standard deviation
Tops						
yield, g/pot	1.37	0.22	0.99	0.26	1.18	0.31
Cd content, μg/g	0.83	0.51	0.50	0.32	0.66	0.45
Roots						
yield, g/pot	1.74	0.45	1.48	0.55	1.61	0.51
Cd content, μg/g	0.24	0.09	0.17	0.09	0.21	0.09
Cd uptake, μg/pot	1.50	0.75	0.72	0.46	1.11	0.73

Results and discussion

On the basis of amounts present in the pots of soil (Table 1), the following average contents were obtained:

	topsoils	subsoils	whole material
org. C, %	4.6	0.9	2.6
clay, % of total weight	34.8	38.0	36.5
CEC, mval/100 g	33.5	24.2	28.5
Fe, mg/g, extractable in ammonium oxalate, pH 3.3	9.4	8.0	8.6

The pots produced on average a dry matter yield of 2.8 g (Table 2), of which the proportion of roots was a little over half. Both the top and root yields of radishes grown on topsoils were on average significantly ($P < 0.05$) greater than yields from subsoils. The native cadmium of the soil produced in the material a cadmium content of the tops at least three times higher on average than that of the roots. Deposition from the air was unlikely in this

Table 3. Response of dry matter yield, its cadmium content and cadmium uptake of radish to cadmium application (400 μg/pot).

	Topsoils n = 25		Subsoils n = 25		Whole material n = 50	
	mean	standard deviation	mean	standard deviation	mean	standard deviation
Tops						
yield, g/pot	− 0.05	0.24	+ 0.01	0.16	− 0.02	0.20
Cd content, μg/g	+11.9	6.5	+35.1	21.3	+23.5	19.5
Roots						
yield, g/pot	− 0.04	0.45	+ 0.07	0.31	+ 0.02	0.38
Cd content, ug/g	+ 3.1	1.6	+ 7.5	6.6	+ 5.3	5.2
Cd uptake, μg/pot	+20.2	10.3	+41.9	20.9	+31.1	19.6

experiment. Of the total cadmium uptake (Table 2) in the whole material, an average of 70 % was present in the aerial parts. Cadmium uptake was significantly greater from the topsoils than from the subsoils ($P < 0.001$).

Addition of cadmium to the soils before sowing had no influence on the yield (Table 3). Differences in yield between the cadmium and no cadmium treatments were probably due to random influences. The variations of the differences were rather large and did not differ significantly from yield variations in the no cadmium treatments (cf. Table 2). Thus, there is some evidence that the latter variations were random, too, rather than dependent on differences between soils.

The increase in cadmium content of the tops was on average 4—5 times as large as the corresponding increase in the root content. In the whole material, radishes took up an average of 7.8 % of the cadmium added. The range of variability was from 1.4 to 11.0 % in the topsoils and from 1.4 to 22.6 % in the subsoils. The increment in cadmium content of both tops and roots of radishes grown on subsoils was significantly greater than the increment for topsoils ($P < 0.01$). Owing to this, also the uptake of applied cadmium was significantly greater from the subsoil than from the topsoil ($P < 0.001$).

Of the quantities determined, cadmium uptake probably provides in theory the best measure of cadmium availability, whose assesment was aimed at. The uptake of applied cadmium was calculated according to the equation $\Delta y = y_1 - y_0 ; y_i = c_{1i} a_{1i} + c_{2i} a_{2i}$, (i = 1, 0), where

Δy = uptake of applied cadmium
y_i = cadmium uptake
c_{1i} = cadmium content of tops
a_{1i} = yield of tops
c_{2i} = cadmium content of roots
a_{2i} = yield of roots
subscript i = 0 with no addition of cadmium
i = 1 after addition of cadmium

Table 4. Correlation coefficients between logarithms of difference in Cd content of tops and of certain soil properties.

	Topsoils n = 25	Subsoils n = 25	Whole material n = 50
organic C	−0.58**	−0.57**	−0.78***
clay	−0.32	−0.55**	−0.23
CEC	−0.63**	−0.58**	−0.58***
exch. H	−0.36	0.03	−0.33*
exch. H/CEC	0.44*	0.56**	0.31*
pH[1])	−0.15	−0.38	−0.15
Fe	−0.32	−0.62**	−0.38*

[1]) untransformed values

It is apparent from the equation that all of the variation in yields is expressed in the calculated values of cadmium uptake. When this variation is large (cf. Tables 2 and 3) and presumably random, it seems likely that the use of the cadmium content as the independent variable instead of the calculated cadmium uptake would allow the attainment of a higher coefficient of determination and a more correct result in the regression analysis. Since the bulk of the cadmium in the plants is contained in the tops, variations were studied of the cadmium content of the tops in particular. The error caused by ignoring the roots is reduced by the fact that the cadmium contents of tops and roots showed a close, positive correlation with each other ($r = 0.956^{***}$). The procedure used thus assumed that top yield is constant for the whole material, and that the top yield contains a constant proportion of the total plant cadmium. The fact that in almost all cases the cadmium content was better correlated than cadmium uptake with other soil characters tested argues in favour of the procedure. The cadmium contents of plants have been used for assessing the availability of soil cadmium by John et al. (1972) and Haghiri (1974).

Correlations between the logarithms of the change in cadmium contents and of characters determined on the soils were rather poor (Table 4). In the whole material, organic carbon was rather well correlated with the dependent variable, but in each of the partial materials the correlation was poorer.

On the basis of pot experiments made with oats, Haghiri (1974) concluded that the depression in cadmium content of the tops associated with an increase in organic matter results solely from an increased cation exchange capacity. The results of the present study do not justify such an conclusion, since the cation exchange capacity accounted for significantly less ($r^2 = 0.33$) of the variation in the cadmium content of the radish than did organic carbon ($r^2 = 0.61$). When organic carbon was taken into account in addition to the exchange capacity, the coefficient of determination was raised from 33 % to 68 % ($P < 0.001$) in the whole material and from 34 % to 44 % ($P < 0.05$) for the subsoils. The increase from 39 % to 48 % for the topsoils was scarcely significant ($0.05 < P < 0.10$).

When the effects of organic carbon, clay, and of cation exchange capacity correlating well with these ($R^2 = 0.80$) were considered simultaneously (Table

5), organic carbon was found to be the most important independent variable in the whole material and in the subsoil material. The coefficients of determination for the alternatives I and II in Tabel 5 did not differ significantly, but the effect of the proportion of exchangeable hydrogen (II) was more consistent than that of the cation echange capacity (I). The elimination of clay, whose correlation with the dependent variable is not significant, led to alternative III, to be considered in more detail below. The coefficient of determination for the whole material was 73 %, or greater than in the topsoil material (48 %) or the subsoil material (59 %).

The regression equations calculated according to alternative III in Table 5 express the following relationships:

topsoils $\Delta c = 116.6 \cdot \frac{x_2^{0.83}}{x_1^{0.74}}$ ($R^2 = 0.48$ for logarithmic transformation)

subsoils $\Delta c = 89.2 \cdot \frac{x_2^{0.72}}{x_1^{0.61}}$ ($R^2 = 0.59$ — » —)

whole material $\Delta c = 99.0 \cdot \frac{x_2^{0.74}}{x_1^{0.69}}$ ($R^2 = 0.73$ — » —), in which equations

Δc = the difference, mg/kg, in cadmium contents between tops from cadmium and no cadmium treatments,

x_1 = amount of organic carbon, g/pot

x_2 = proportfon oi hydrogen of exchangeable cations.

The exponentials (regression coefficients after logarithmic transformation) of all the equations given were significant. The high hydrogen proportion and the low amount of organic carbon thus represent a large increase in the cadmium content of the tops. The simplest explanation is that the increase in cadmium content is directly proportional to the proportion of exchangeable hydrogen, and inversely proportional to the amount of organic carbon. While this hypothesis regarding exchangeable hydrogen could not be disproved, both in the subsoil material and in the whole material the exponential of the amount of organic carbon was significantly smaller than unity. This indicates that a given relative increase in organic carbon corresponds on average to a smaller relative decrease in cadmium content response of radish tops.

John et al. (1972) have also established that the cadmium content of radish tops depends upon the content of soil organic matter and soil acidity expressed as pH measured on a suspension of soil in salt solution. In their material, an additional independent variable was provided by a separate determination of the soil capacity for retaining cadmium from a solution. Part of the variation accounted for by this new variable would otherwise have been explained by organic matter and pH. In the material of John et al. (1972), the iron soluble in dilute mineral acids raised the coefficient of determination considerably. In the material of the present study, however, iron extracted from the soil with acid ammonium oxalate at pH 3.3 had no significance as an independent variable after the effects of organic carbon and exchangeable hydrogen had been eliminated. The present material is not strictly comparable with that of John et al. (1972), as they determined iron by a different method. The iron content in their material averaged about 80 mg/kg, in the present material 8 600 mg/kg.

Table 5. Partial correlation coefficiants (r) and coefficient of determination (R^2) between increase in cadmium content in radish tops (y) and organic carbon (1), clay fraction (2), cation exchange capacity (3) and hydrogen percentage of exchangeable cations (4) in soil (logarithmic transformation).

	Topsoils n = 25	Subsoils n = 25	Whole material n = 50
I. Omitting effects of hydrogen percentage			
$r_{y1.23}$	−0.34	−0.45*	−0.69***
$r_{y2.13}$	0.00	−0.26	−0.11
$r_{y3.12}$	−0.35	−0.01	−0.20
$R^2_{y.123}$	0.48**	0.48**	0.68***
II. Omitting effects of cation exchange capacity			
$r_{y1.24}$	−0.59***	−0.60**	−0.84***
$r_{y2.14}$	−0.05	−0.04	−0.03
$r_{y4.12}$	0.33	0.46*	0.42**
$R^2_{y.124}$	0.48**	0.59***	0.73***
III. Omitting effects of clay fraction and cation exchange capacity			
$r_{y1.4}$	−0.59**	−0.63**	−0.83***
$r_{y4.1}$	0.47*	0.63**	0.56***
$R^2_{y.14}$	0.48***	0.59***	0.73***

The higher coefficient of determination in the whole material than in either of the component materials is due to differences in the partial correlation coefficients incorporating organic carbon. On the basis of its level of organic carbon, the material could be naturally divided into two components, whose mean responses of the cadmium content of the tops to added cadmium were different (cf. Table 3). This difference in means is not necessarily due solely to a difference in the amount of organic carbon between the component materials, but may also be caused by some character not determined here.

A larger proportion of the variation in increase of the cadmium content of radish tops could be accounted for in the subsoil material than in the topsoil material. It is possible that some character common to the plough layer and subsoil and not investigated here was influencing the results. For these reasons, an attempt was made to improve the coefficient of determination in the topsoil material by taking into account as an independent variable the increase in cadmium content of radishes grown in the corresponding subsoil sample. This measure increased significantly the coefficient of determination, from 48 % to 57 %. The nature of the common character was quite unresolved. When the increase in cadmium content of radishes grown in subsoil was replaced by the proportion of hydrogen of subsoil exchangeable cations as an independent variable, the coefficient of determination did not fall significantly (to 55 %), but in any case this latter variable was not significant ($0.05 < P < 0.10$). It is conceivable that the proportion of exchangeable hydrogen in the subsoil characterizes soil acidity under constant conditions when organic carbon does not cause interference by its variations which are nevertheless apparent in the plough layer.

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SELOSTUS

Maahan lisätyn kadmiumin käyttökelpoisuus retiisille astiakokeessa

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Tutkimuksessa pyrittiin selvittämään eräiden maan ominaisuuksien vaikutus maahan lisätyn kadmiumin käyttökelpoisuuteen kasville. Tutkitut ominaisuudet olivat orgaaninen hiili, saves, kationinvaihtokapasiteetti, vedyn osuus vaihtuvista kationeista ja happameen ammoniumoksalaattiin liukeneva rauta.

Maanäyteaineiston muodostivat 25 paikasta etelä- ja itä-Suomesta otetut näytteet. Jokaisesta paikasta otettiin näyte kyntökerroksesta ja jankosta. Kasvihuoneessa järjestetyssä astiakokeessa määritettiin maihin sekoitetun kadmiumnitraatin (0.4 mg Cd/400 ml maata) vaikutus viiden viikon ikään kasvatetun retiisin kadmiumpitoisuuteen ja kadmiuminottoon. Lisätystä kadmiumista retiisin laskettiin ottaneen yhteensa 1.4—22.6 %. Maanpäällisten osien kadmiumpitoisuuden nousun (Δ c) ja koeastian sisältämän orgaanisen hiilen määrän (x_1) sekä vaihtuvan vedyn osuuden (x_2) välillä todettiin yhteys $\Delta c = k \cdot \frac{x_2^{b_2}}{x_1^{b_1}}$. Lisäksi osoitettiin, että $0 < b_1 < 1$ ja $0 < b_2 \leq 1$. Koko 50 näytteen aineistossa, jossa Δ c vaihteli 2.2—94.9 mg/kg Cd, tämän mallin logaritmimuunnos selitti 73 % vaihtelusta. Kyntökerrosnäytteiden aineistossa, jossa selvitysaste oli huonompi (48 %) kuin jankkoaineistossa (59 %), vaihtelusta pystyttiin selittämään enemmän (57 %) ottamalla lisäksi selittävänä muuttujana huomioon retiisin kadmiumpitoisuuden nousu vastaavassa jankkoaineistossa. Tämän pääteltiin osoittavan, että kyntökerrokseen lisätyn kadmiumin käyttökelpoisuus riippui orgaanisen hiilen ja vaihtuvan vedyn osuuden lisäksi jostakin ominaisuudesta, jota ei ollut määritetty kyntökerrosnäytteistä ja joka oli korreloitunut jankossa vaikuttavien lisätyn kadmiumin käyttökelpoisuutta säätävien tekijöiden kanssa.

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